REACTIONS OF DIFLUORAMINE WITH LEWIS ACIDS*

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INTRODUCTION

Craig[1] has recently reported the results of a study of the reactions of several nitrogen-fluorine compounds with Lewis acids. As was expected, he found that all of the compounds studied were extremely weak bases, difluoramine and its methyl derivative being among the strongest. We are prompted to report some of our data on the reactions of the latter compounds with certain other strong acids.

With the purpose of obtaining new nitrogen fluorine type oxidizers, we have been studying the possibility of preparing difluorammonium salts, $H_2NF_2^+X^-$, and of introducing difluoramino groups into compounds of light metals, such as $Al(NF_2)_3$. To this end, the reactions of difluoramine and methyl difluoramine with certain acids have been studied.

RESULTS AND DISCUSSION

Difluoramine, HNF_2, and methyl difluoramine, CH_3NF_2, have been shown to form isolable complexes with BF_3, BCl_3, and SO_2, and in some cases dissociation data could be obtained. It is evident from Craig's work that usable thermodynamic data will be available only with the strongest acids. The problem is further complicated by the tendency for irreversible decomposition to occur in most of these systems. The acids chosen for this study included the protic acids, hydrogen chloride and trifluoroacetic acid, the metal alkyls, trimethyl aluminum and trimethyl gallium, and sulfur trioxide, one of the strongest gaseous Lewis acids known. Pressure-composition studies were made of these systems in the usual manner, to detect adduct formation or other condensed phase interactions.

The pressure-composition diagrams of the difluoramine-protic acid systems did not indicate compound formation. With HCl, HNF_2 was miscible in all proportions, with large positive deviations from Raoult's Law, while with CF_3CO_2H, partial solubility was


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[1]A.D. Craig, Inorg. Chem. 3, 1628 (1964).

observed, and the solution was ideal. The stronger base, methyldifluoramine, was also miscible with HCl in all proportions, with large negative deviations from Raoult's Law. At the lowest temperature, -127°C, a plateau was obtained, indicating the formation of a 1:1 adduct. This is to be expected, since the methyl derivative should be a significantly stronger base.

Both fluoramines from 1:1 adducts with SO_3, although the adducts probably do not have similar structures. The pressure-composition diagram of the HNF_2-SO_3 system has a minimum at a mole fraction of 0.4, and an inflection at about 0.5. Whether or not these observations indicate the formation of a 1:1 and a 1:2 compound is difficult to decide, due to the fact of slow decomposition of the product, and of the difficulty of obtaining true equilibrium in systems containing condensed SO_3. N.m.r. spectroscopy supports the structure, F_2NSO_2OH (difluorosulfamic acid). The CH_3NF_2-SO_3 system is more conventional. A good pressure plateau, and a sharp pressure rise past a mole fraction of 0.5 indicate the formation of a 1:1 compound.

Irreversible decomposition interferes with pressure-composition studies of these amines with trimethyl aluminum. Coordination compounds are probably intermediates, but no evidence was obtained for their existence. The reaction of trimethylaluminum with difluoramine produces methane, even at -80°C, and often results in explosions. The reaction appears to be the usual elimination which occurs with many hydrogen-containing bases:

$$(CH_3)_3Al + HNF_2 = (CH_3)_2AlNF_2 + CH_4$$
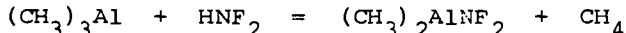
Although this reaction renders the system useless for the purpose of obtaining thermodynamic data on the basicity of difluoramine, it does suggest the possibility of a new oxidizer, $Al(NF_2)_3$. In an attempt to obtain this compound by the use of an excess of difluoramine, twofold substitution was obtained, presumably producing $CH_3Al(NF_2)_2$, although the compound has not been definitely identified.

The reaction of equilimolar amounts of methyl difluoramine with trimethylaluminum produces two moles of methane and a smaller amount of HCN. The reaction is evidently the decomposition of the amine:

$$CH_3NF_2 = HCN + 2 HF$$
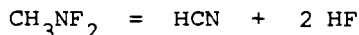
followed by reaction of the HF with trimethylaluminum, liberating methane.

The difluoramine-trimethylgallium system was studied briefly, in an attempt to isolate a coordination compound. No evidence was obtained for such a compound from the pressure-composition data, and the mixture obtained was easily resolved into its components by simple trap-to-trap distillation. At room temperature, however, the elimination of methane occurred, very slowly.

EXPERIMENTAL

A standard Stock-type high vacuum line was used, except for experiments with SO_3 or CH_3NF_2. In these cases stopcocks lubricated with Kel F-90 grease were used, and pressures were measured with a Bourdon gauge.

The commercially available materials, HCl, $(CH_3)_3Al$, and CF_3CO_2H, were purified by trap-to-trap distillation in the vacuum line. SO_3 was generated as needed by passing the vapors from a sample of "Sulfan B" over a P_2O_5 column. Trimethyl gallium was prepared by the reaction of gallium with dimethyl mercury at 130°C. Difluoramine was prepared by the thiophenol reduction of tetrafluorohydrazine.[2]

The HNF_2-HCl System

A pressure-composition study of the system HNF_2-HCl was performed by adding successive small samples of HCl to a sample of HNF_2 held at constant temperature by an appropriate "slush" bath. The data obtained at -112, -127, and -138°C indicated that the two compounds are miscible in all proportions. Deviations from Raoult's Law were positive, indicating no compound formation in the condensed phase.

The CH_3NF_2-HCl System

The pressure composition data were obtained in the same manner as above, except that the mercury-free system was used. In an early experiment with this system, the mercury manometer rapidly became fouled in contact with the mixture of gases. In later exploratory experiments, however, no apparent reaction occurred in several days between a mixture of these gases and mercury in a sealed tube. However, one of these tubes exploded when shaken gently. The previous fouling of the manometer may have been caused by some impurity in the difluoramine.

The pressure-composition diagrams show large negative deviations from Raoult's Law at -95, -112, and 127°C, and at the lower temperature, a plateau indicating the formation of a 1:1 compound.

The HNF_2 - CF_3CO_2H System

Because of the corrosive nature of sulfur trioxide and the tendency of the low-melting form to undergo transition to more highly polymerized forms, it is a rather difficult material to use in an equilibrium process. It was not possible to obtain reproducible saturation pressures for this system by adding HNF_2 to SO_3 at low temperatures. However, at 0°C, a liquid was obtained over the whole composition range studied (up to x = 0.6) and equilibrium could be obtained, although slowly. The pressure-

[2] J.P. Freeman, A. Kennedy and C.B. Colburn, J. Am. Chem. Soc. __82__, 5304 (1960).

composition diagram shows a minimum at X_{HNF_2} = 0.4, and an inflection at about 0.5, with a sharp increase in pressure beyond that. Possibly, a 2:1, as well as a 1:1 compound is formed.

The proton and F^{19} n.m.r. spectra indicated only single frequencies for hydrogen and fluorine, neither of which was split, indicating that the hydrogen is no longer on the nitrogen atom. These observations are consistent with the structure F_2NSO_2OH, but not with the coordination compound, $HNF_2:SO_3$.

Slow decomposition of the product occurs at room temperature, the volatile products being N_2F_4 and SO_2. The reaction is probably the following:

$$2\ NF_2SO_2OH \longrightarrow N_2F_4 + SO_2 + H_2SO_4$$
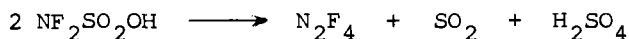
The CH_3NF_2 - SO_3 Systems

The CH_3NF_2 - SO_3 system was examined in a similar manner. At -63.5°C, the pressure-composition diagram indicated only slight solubility of SO_3 in the difluoramine. At -45.2°C, however, the curve is typical of a system in which a 1:1 adduct is formed. The adduct is a white solid, melting at about -10°C, to a clear, colorless liquid. At about 0°C, an exothermic reaction occurs, the liquid becomes yellow, and HCN and SiF_4 are found in the volatile products.

The HNF_2-$(CH_3)_3Al$ System

When attempts were made to study the pressure composition curve of this system, it was soon discovered that explosions occurred whenever the HNF_2 is added in such a manner that the liquid can contact the condensed $(CH_3)_3Al$, even at low temperatures. When successive small amounts of gaseous HNF_2 are added to a reactor containing the alkyl at -80°C, methane is slowly evolved. In one such experiment, 9.5 cc of $(CH_3)_3Al$ was condensed in a small tube at -80°C, and small amounts of HNF_2 added, taking care to keep the total pressure below 25 mm. The methane, which was pumped out each time between additions, totaled 12.1 cc before an explosion occurred.

In an attempt to moderate the reaction, and to obtain more extensive substitution, 9.9 cc of $(CH_3)_3Al$ was dissolved in 5 ml dry isopentane, and 30.8 cc HNF_2 was allowed to distill into the solution at -80°C. The evolution of methane was very slow, even when the solution was brought to room temperature. A total of 19.4 cc CH_4 was obtained over a period of three days, very close to that required for a 2:1 reaction. No new volatile product was found. The yellow solid residue, presumably $CH_3Al(NF_2)_2$, liberated only a trace of iodine when dissolved in a KI solution.

CH_3NF_2-$(CH_3)_3Al$ System

In a single experiment, 9.8 cc CH_3NF_2 and 9.9 cc $(CH_3)_3Al$ were combined and allowed to thaw. Vigorous effervescence began as soon as an appreciable pressure was observed, and was soon

complete at room temperature. The only volatile products were 19.7 cc CH_4 and 3.5 cc HCN.

The HNF_2-$(CH_3)_3Ga$ System

HNF_2 and $(CH_3)_3Ga$ were combined in a small reactor and thawed. The reaction to form methane was very slow, about 2/3 mole being produced overnight at room temperature. No explosion occurs, even in the presence of large excess of HNF_2. A preliminary pressure-composition study did not reveal an adduct at $-?.5°C$ or $-45.2°C$. Distillation of the mixture through a $-80°$ trap separated the components almost completely in one pass.